

Description

Piezoelectric Device

The invention concerns a piezoceramic device with a stack of at least two ceramic layers and an electrode layer arranged between two ceramic layers and a method to its production.

Such piezoceramic devices therefore include several, particularly many layers (multilayer devices); they are for example utilizable as actuators in piezo stacks, by obtaining a low-inertia mechanical excursion of comparably high force by the voltage control or as bending elements, by causing a high mechanical excursion of less force by the voltage control, or they permit the production of high electrical voltages resp. serve the detection of mechanical or the production of acoustic vibrations with the relevant devices.

Technical solutions up to now are based on predominantly ceramic masses of the Perovskite structure type of the general formula ABO_3 , whereby the piezoelectrical characteristics are brought to bear in the ferroelectrical condition. Lead zirconate titanate ceramics $Pb(Zr_{1-x}Ti_x)3 = PZT$ modified by certain additives, have been shown particularly advantageous, whose combination is tailored to the so-called morphotropic phase interface of two co-existing ferroelectrical phases, a tetragonal and a rhombodic phase. Between the ceramical layers, produced according to the typical methods of the ceramic foil technology, there are precious metal internal electrodes applied by screen printing, for example Ag/Pd in the molar ratio 70/30. At up to several hundred electrode layers, the devices are thereby burdened with substantial costs. The precious metal electrodes permit to eliminate thermically the dispersers and binders as well as the other organic additives used in the process of the ceramic foil production, and also the organic components of the screen printing-metal paste of the multilayer stacks by air depolymerisation and oxydation, so that afterwards a sinter condensation at approx. 1100 to 1150°C is made possible, without causing reduction effects, for example conditioned by residue carbon left-overs, which negatively influence the characteristics of the ceramics because of reduction reactions.

Tests with La₂O₃ or Nd₂O₃ doped Pb(Zr,Ti)O₃ - ceramics are particularly documented in the literature, for example of G.H. Haertling in the journals American Ceramic Society Bulletin (43(12), 113-118 (1964) and Journal of the American Ceramic Society 54, 1-11 (1971) as well as in the monographies "Piezoelectric Ceramics", Academic Press, London and New York (1971) of B. Jaffe, W.R. Cook and H. Jaffe as well as of Y. Xu. In "Ferroelectric Materials and their Applications", Elsevier Science Publishers, Amsterdam (1991).

La₂O₃ – resp. Nd₂O₃ – additives induce the production of cation vacancies on the Pb positions of the crystal structure, but at the same time increase thereby the tendency to act as donors, particularly at insufficient oxygen partial pressure, which can lead to a depression of the insulating resistance and a rise of the dielectrical losses, i.e. the sensitivity of the ceramic towards reduction is increased. At the same time they stabilize the tetragonal phase, and the kinetics of the orientation of the domains in field direction at the polarity are facilitated, i.e. the electro mechanical characteristic behaviour of a so called "soft piezoceramic" is influenced positively by such additives for this application. For an advancement of the sinter condensation and prevention of evaporation losses at PbO of the ceramic, a low PbO surplus at the originally weighed-in composition is generally considered. It was talked in detail about the connection between the doping level by La₂O₃ in a Pb(Zr_{0,47}Ti_{0,53})O₃-ceramic supplied with 3 molar-% PbO surplus and the sinter behaviour as well as the structure formation

associated with this and the electro magnetic characteristics like coupling factor and dielectricity constant including the curie temperature, the maximum temperature for ferroelectrical and with it also piezoelectrical behaviour, in the journal of electroceramics 2(2), 75-84 (1998) by M. Hammer and M. Hoffmann.

Ceramic masses with bismuth oxyde in place of lead oxyde were also taken into consideration, for example $(\text{Bi}0.5\text{Na}0.5)\text{TiO}_3\text{-KNbO}_3\text{-BiScO}_3$ of T. Takenaka, H. Nagata in proceedings of the 11th Inter. Symp. Appl. of Ferroelectrics, Montreux 1998, IEEE 98CH36245, 559-562 (1998), or $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ was combined with BiScO_3 and/or BiInO_3 . All these ceramics are based on Perovskite mixed crystal phases, which in combination with Ag/Pd internal electrodes produce a relatively positive characteristic behaviour for the purpose of piezostack, when the debinding, i.e. the removal of the binder or binders, and the sinter condensation is air-done.

Piezoelectrical ceramic masses of the general composition $(\text{Pb}_{1-x-\alpha-y}\text{Sr}_x\text{Na}_{\alpha}\text{M}_y)\text{a}(\text{Nb}_b\text{Y}_c\text{Cr}_d\text{Co}_e\text{Sb}_f)\text{TgZr}_{1-f-g}\text{O}_3$ are protected in the print US 5 648 012, which are distinguished by high electromechanical coupling factors, whereby M is at least a rare earth metal of La, Gd, Nd, Sm and Pr and the parameter areas $0,005 \leq x \leq 0,08$, $0,002 \leq y \leq 0,05$, $0,95 \leq \alpha \leq 1,105$, $0,47 \leq b \leq 0,70$, $0,02 \leq c \leq 0,31$, $0,11 \leq d \leq 0,42$, $0,01 \leq e \leq 0,12$, $0,02 \leq f \leq 0,15$, $0,46 \leq g \leq 0,52$, $0 \leq \beta \leq 0,13$ as well as $b+c+d+e+\beta=1,00$ are known.

The print DE 9700463 for the production of green foils for piezoceramic multilayer devices is as well based on a piezoceramic powder of the type PZT, to which a stoichiometric surplus of a heterovalent rare earth metal up to a content from 1 to 5 molar-% and a stoichiometric surplus of an additional 1-5 molar-% lead oxyde is added. In addition it is documented in this print, that Ag^+ -ions from the area of Ag/Pd - internal electrodes diffuse exactly in such a portion into the ceramic layers of the multilayer devices, that the by the heterovalent doping produced cation vacancies are occupied and in this way will result in a filled up Perovskite structure, like for example $\text{Pb}_0,99\text{Ag}_0,01\text{La}_0,01\{\text{Zr}_0,20\text{Ti}_0,36(\text{Ni}_{1/3}\text{Nb}_{2/3})_0,34\}\text{O}_3$ or $\text{Pb}_0,96\text{Ag}_0,02^{Nd}\text{O},02(\text{Zr}_0,54,\text{Ti}_0,46)\text{O}_3$. In the latter case a piezoceramic is produced with a comparatively high Curie temperature for applications up to 150°C. It is also well founded that the composite solidity between the Ag/Pd internal electrode (70/30) and the ceramic as well as the corn growth at the sintering are positively influenced by building silver into the ceramic.

To prevent the disadvantage of the high costs of such piezoceramic multilayer elements on the basis of a ceramic of a PZT-type, it is possible, to provide an application of copper in place of the expensive Ag/Pd - internal electrodes. Thermodynamic data has shown, that PZT-ceramic is for example at 1000°C under a certain very low oxygen partial pressure of $< 10^{-2}$ is not reduced and metallic copper stays under these conditions stable as well, i.e. doesn't oxidize.

From the print US 5,233,260 piezoactuators are known, which are not carried out in a monolithic way though. The ceramic layers are rather separately sintered and only then stacked and agglutinated. This production method is correspondingly costly. Furthermore, these piezoactuators have the disadvantage, that the used glue has a negative effect on the electrical characteristics.

That this statement is also accurate on a donor doped ceramic, is proven by an examination of Cao and employees in the journal of the American Ceramic Society 76(12) 3019 (1993), wherein Cu foil is laid between pre-made ceramic segments $\text{Pb}_0,988(\text{Nb}_0,024\text{Zr}_0,528\text{Ti}_0,473)\text{O}_3$ and such a multiple sandwich arrangement is subject to

an examination to a sintering at 1050°C under vacuum. The good composite between the ceramic and Cu internal electrode and the absence of the migrational effects, like they are observed at Ag electrodes on air, are emphasized. But such a way of process does not correspond to the requirements of an efficient production, like the foil multilayer technology makes it possible, and is not apt for a mass production.

Kato and colleagues describe in Ceramic Transactions Vol. 8, pages 54-68 (1990) the production of multilayer condensators with ZSU specifications on the basis of ceramics of the general formula (Pba-Cab) $(Mg_{1/3}Nb_{2/3})_xTi_y(Ni_{1/2}W_{1/2})_{zO_2+a+b}$ ($a+b > 1$, $x+y+z=1$) with Cu internal electrodes, whereby a copper oxyde screen-printing paste is used. Air-debinding is thereby made possible. The carbon formation, which would inevitably come into effect under nitrogen at a well-tolerated metallic copper with oxygen partial pressure and afterwards at the sinter condensation lead to a reductive degradation of the ceramic with Cu/Pb -alloying production – the eutectic melting point lies at $T_S = 954^\circ\text{C}$ – is thereby avoided. After the debinding, the sinter condensation is then carried out at 1000°C by additional dosage of hydrogen at a oxygen partial pressure, 10^{-3} Pa and the copper oxyde is reduced to copper under these conditions. The process is interference-prone because of the shrinkage during the reduction from copper oxyde to copper and the from this resulting tendency to delamination and has up to now not been technologically converted into products.

In the print DE 197 49 858 C1, at the production of COG – multilayer condensators with Cu -internal electrodes on the basis of a ceramic mass with the general composition $(BaI1-yPby)6-xNd8+2x/3Ti18054 + z$ m-% Ti0w + p m-% Glas at lower PbO content ($0,6 \leq x \leq 2,1$; $0 < y < 0,6$, $0 < z < 5,5$ and $3 < p < 10$) a sufficient elimination of the organic components by feeding steam into the nitrogen flux with $< 10^{-2}$ Pa oxygen partial pressure at temperatures up to 680°C and the sinter condensation at 1000°C is reached by apt glass frit additives. The method could be successfully applied in the DE 19841487 on COG-multilayer condensators with the PbO free ceramic $BaI6-x(SmyNd1-y)8+2x/3Ti18054 + p$ weight -% glass frit ($1 < x < 2$, $0,5 < y \leq 1,0$ and $3 < p < 1$).

Piezoceramic devices in a monolithic multilayer built with copper-containing internal electrodes on the basis of a piezoceramic of any composition, preferably on the basis of a Perovskit ceramic of the PZT type are intended according to the invention. The modification by mixed crystal formation by building in cations on the A positions as well as by substitution of the B-cations by apt other cations or combinations of cations can be thereby achieved, and the from the production of multilayer condensators known methods of ceramic foil technique as well as the common sintering of the ceramic layers with the for example by screen printing alternatively brought in internal electrodes of copper or a mixture of Cu with ceramic resp. other metallic additives can be applied.

Such piezoceramic multilayer devices can be realized for example as actuators by an apt process guide, by which the debinding of the green foil stacks is carried out by steam by avoiding the oxydation of the Cu-containing internal electrodes. The following sinter condensation to a monolithic multilayer device can be carried out in an advantageous ways at already 1000°C, this means below the melting temperture of the copper.

Advantageous further formations of the inventions are separately marked.

The advantage of the invention lies therein, that for a PZT ceramic mass, copper-containing internal electrodes are applied in place of the so far normally used Ag/Pd internal electrodes (70/30) on the basis of the multilayer foil technique, whereby the practically complete

debinding can be successfully done before inserting the sinter condensation under inert conditions in such a way that a lot of steam is supplied to the inert atmosphere during the debinding and permits only a set oxygen partial pressure, which leaves the Cu-containing internal electrodes intact. Thereby the conditions are being created, that during the process of the following sinter condensation, piezoactuators with optimal characteristic results of the ceramic can be obtained, which don't take second place to the ones which were under analogue conditions separated from the Cu-containing electrode layer or also air-sintered piezo ceramic layer of the corresponding composition resp. do even better.

A device is advantageous, at which cations are built in on A-positions of the ceramic and at which cations on B-positions are replaced by apt other cations or combinations of cations. For example, on A-positions of the ceramic can be built in bivalent metal cations M^{II} . These can be selected for example from a group of elements, which contains barium, strontium, calcium, copper and bismuth. Bivalent metal cations M^{II} from a group of elements which contains scandium, yttrium, lanthanum or also from group of lanthanides can be considered for the A-positions of the ceramic.

Further, monovalent cations can be built in on the A-positions of the ceramic, which are selected advantageously and from a group of elements which contains silver, copper, sodium and potassium.

In addition it is also possible, to build in combinations of bivalent metal cations M^{II} and monovalent cations on A-positions.

Furthermore a device is advantageous, where to the partial substitution of the quadrivalent cations Zr and Ti on the B-positions of the ferroelectrical Perovskite ceramic, combinations of mono- and quintvalent metal cations M^I, M^V , with $M^I = \text{Na}, \text{K}$ and $M^V = \text{Nb}, \text{Ta}$ or two- and quintvalent metal cations $M^{II}_{1/3}M^V_{2/3}$ with $M^{II} = \text{Mg}, \text{Zn}, \text{Ni}, \text{Co}$ and $M^V = \text{Nb}, \text{Ta}$ or three- and quintvalent metal cations $M^{III}_{1/3}M^V_{2/3}$ with $M^{III} = \text{Fe}, \text{In}, \text{Sc}$, heavier lanthanide-elements and $M^V = \text{Nb}, \text{Ta}$ or combinations $M^{III}_{2/3}M^V_{1/3}$ with $M^{III} = \text{Fe}, \text{In}, \text{Sc}$, heavier lanthanide-elements and $M^V = \text{Nb}, \text{Ta}$ or combinations $M^{VI}_{1/4}M^{VI}_{1/4}$ with $M^{VI} = \text{Mg}, \text{Co}, \text{Ni}$ and $M^{VI} = \text{W}$ are put in.

Further it is advantageous, if the composition of the ceramic with the general formula $\text{Pb}_{1-x-y}^{\text{SE}} \text{x}^{\text{Cu}} \text{y}^{\text{V}}, \text{x}/(2^z 0,54 - z^0,46 + z)^0,3$ corresponds with $0,01 < x < 0,05$ and $-0,15 < z < +0,15$ as well as $0 < y < 0,06$, whereby SE is a rare earth metal and V a vacancy, and whereby a PbO-surplus is set from 1 up to maximally 5 molar-%.

On top of this the ceramic can contain an additive of CuO.

The invention includes the realization, that the by donors, for example, a rare earth metal, doped piezo ceramic on the basis of PZT because of the formation of cation vacancies on the A-positions of the Ferovskit structure, for example according to the composition $\text{Pb}^{II}_{0,97} \text{Nd}^{III}_{0,02} \text{V}^{\prime\prime} \text{Pb}_{0,01}^{\prime\prime} (2^z 0,54 - z^0,46)^0,3$ (V' means here an empty space), develops a certain affinity, to absorb copper from the internal electrodes, without destroying them, by elimination of equivalent PbO-shares, whereby the latter combination acts as a sinter aid and up to some percentage of PbO is separately added to the ceramic anyway.

The sinter condensation is supported by the known mobility of the copper ions, and leads by the copper migration to a solid adhesion between the electrode layer and ceramic, so that delaminations can be effectively avoided this way.

It is of advantage, to already add some CuO within the limits $0 < y < 0,15$ to the original mixture of the used recipe for piezostacks for example on the basis of PZT with Cu-internal electrodes corresponding to the general formula $Pb_{1-x-y}SE_{x/2}Cu_yV_{(x/2)(1-x-y)}(Zr_{0,54-z}Ti_{0,46+z})O_3$ with $0,005 < x < 0,05$ and $-0,15 < z < +0,15$ (SE = Rare Earth Metal). The piezoelectrical characteristics, like the high value for the electromechanical coupling factor can be maintained at corresponding adjustment of the parameter z to the morphotropic phase interface.

The invention is explained in more detail by the following models and five figures belonging to them.

The from TiO₂, ZrO₂ resp. from a mixed precipitation produced precursor (Zr, Ti)O₂ and PbCo₃ resp. Pb₃O₄ and dopants like La₂O₃ or from another oxyde of the rare earth metals and if necessary an additive of CuO based raw material mixture is set in its composition on the morphotropic phase interface, a PbO-surplus of maximally 5 % to support the sinter condensation, for even distribution of the component undergoes a grinding step in diluted suspension an is calcinated after the filtering and drying at 900 to 950 °C. Thereby the piezoceramic Perovskite-mixed crystal phase is built. To obtain sinter condensation in 2 to 4 hours at already 1000 ° below the melting temperature of copper, a pulverization to a medium grain size $< 0,4 \mu m$ is necessary. The sinter activity of the powder shows then to be sufficient, to guarantee a condensation of $> 96\%$ of the theoretical density at both sufficient grain growth and adequate mechanical solidity in the ceramic structure.

The finely ground powder is suspended to a diluted slip with approx. 70 m-% solid substance content by use of a disperger, this corresponds to approx. 24 vol.-%. For this, the for an optimal dispersing just necessary dispergator portion is separately determined in a series of tests, which can be recognized by obtaining a viscosity minimum. For the formation of the piezoceramic-green foils approx. 6 m-% of a commercial binder is added to the dispersed suspended solids, which is thermohydrolytically degradable. For this a diluted polyurethane dispersion shows to be of advantage. It is mixed in a disperse mill and receives this way a for the process of "foil-pulling" resp. for the production of a spraying granular apt slip.

Discoid green compacts, produced from the granular, or small square multilayer printed boards "MLP", produced by stacking and laminating from the 40 to 50 μm thick green foils without print with Cu-electrode paste, can be debindered up to a residue carbon content of 300 ppm in a H₂O-steam containing inert atmosphere at a defined oxygen partial pressure, which fulfills the condition of the coexistence of PbO resp. Bi₂O₃-containing piezoceramic and copper.

The hydrolytical separation of the binder takes place for the main part at a very low temperature of 200 ± 50 °C at a steam partial pressure bigger than 200 mbar. The oxygen partial pressure is set to a value, which is well-tolerated with the Cu-containing electrodes. This is done by gettering the oxygen from the flow of gas at big surfaces of Cu or by adding of H₂. During the debinding by oxydation at the sample it drops, but the flow of gas avoids a damage to the ceramic. Although the electrode layers support the debinding, because preferred paths for a binder transportation is created by them, there is still a considerable debinding time necessary, particularly for the actuators with 160 electrodes (measurements 9,8 * 9,8 * 12,7 mm³).

The invention enables herewith the production of actuators with more than 100 internal electrodes, which has the advantage of a highly obtainable actuator-excursion.

Examples for a debinding control are found in table 1 by indicating the residue carbon content of the obtained devices. The dew point for steam of both debinding programs lies at 75°C, the partial pressure of the steam corresponds to 405 mbar.

Table 1: Debinding of ceramic samples MLP and actuators

Profile	Conditions (R: ramp, H: holding time)	Samples	C
EK 1	R: 30 K/h H: 220 °C/10 h R: 30 K/h H: 500 °C/20 h, at 100 l/h N ₂ , 30 g/h H ₂ O, with Cu-gettering	Ceramic samples MLP	240
EK 2	R: 30 K/h H: 220 °C/40 h R: 30 K/h H: 500 °C/20 h, at 100 l/h N ₂ , 30 g/h H ₂ O, with Cu-gettering	Actuator 160 electrodes	300 +30

The soaking time at 220 °C is prolonged to 40 h for actuators with 160 layers (EK 2). Afterwards a condensation of the ceramic at 1000 °C without detrimental reductive degradation is succeeded with the residue carbon of 300 ± 30 ppm in the indicated sinter profile.

Figure 1 shows the temperature control during the debinding and sintering. The steam partial pressure supplied with the nitrogen flux corresponding to a dew point of 75°C is indicated as well.

At such debinded PZT-ceramic samples the sinter condensation is succeeded at 1000°C, without creating a reductive degradation of the ceramic. The dielectrical and especially the piezoelectrical characteristics of the obtained samples with the measurements of approx. 10.10 mm² and 0,7 resp. 2 mm consistency are measured after contacting by sputtering of Au-electrodes and compared with the air-debindered and at 1130 °C sintered samples of the same geometry.

For air-sinterings of ceramic samples MLP without internal electrodes with the composition Pb_{0,97}Nd_{0,02}V_{0,01}(Zr_{0,54}Ti_{0,46})O₃ and under inert conditions, whereby the latter correspond to the requirements of a common sintering with copper, the results of the electrical measurings are compiled in table 2, the ones of the polarized samples in tables 3 to 5. In addition, the codes of a CuO-doped ceramic mass during sintering under inert conditions are quoted.

Table 2: Characteristics of square ceramic samples MLP (edge length 1, consistency h): Samples (a), (b) and (c) with the composition Pb_{0,97}Nd_{0,02}(Zr_{0,54}Ti_{0,46})O₃. Sample (d) with the composition Pb_{0,96}Cu_{0,02}Nd_{0,02}(Zr_{0,54}Ti_{0,46})O₃ (a) powder pre-ground to a medium grain size d_{50%}=0,53 µm, air-sintering at 1120°C; (b), (c) and (d) powder finely ground to a medium grain size d_{50%}=0,33 µm, air-sintered (b) at 1000°C resp. (c) and (d) at 1000°C under N₂/H₂O-steam.

Sample MLP	h/mm	1/mm	C/nF	ε	Tan δ	R ₁₅ /Ω	ρ/Ωcm
(a)	0,59±0,02	10,8±0,1	2,20±0,05	1268±30	2,1±0,1%	1 * 10 ¹¹	2 * 10 ¹²
(b)	0,70±0,01	10,6±0,1	1,60±0,03	1137±58	2,8±0,2%	2 * 10 ¹¹	3 * 10 ¹²

(c)	$0,71 \pm 0,02$	$11,0 \pm 0,8$	$1,62 \pm 0,07$	1132 ± 81	$2,8 \pm 0,6\%$	$5 * 10^9$	$9 * 10^{10}$
(d)	$0,70 \pm 0,01$	$11,3 \pm 0,1$	$1,92 \pm 0,01$	1196 ± 8	$1,9 \pm 0,3\%$	$7 * 10^{10}$	$1 * 12^{12}$

Table 3: Characteristics of square ceramic samples MLP (edge length 1, consistency h) with the composition according to table 2 after the polarity with 1200 V (a) resp. 1400 V ((b) and (c) and (d)).

Sample MLP	h/mm	l/mm	C/nF	ϵ	Tan δ	R_{15}/Ω	$\rho/\Omega \text{cm}$
(a)	$0,59 \pm 0,02$	$10,8 \pm 0,1$	$2,54 \pm 0,13$	1460 ± 134	$1,9 \pm 0,1\%$	$1 * 10^{11}$	$2 * 10^{12}$
(b)	$0,70 \pm 0,01$	$10,6 \pm 0,1$	$1,70 \pm 0,03$	1207 ± 58	$2,1 \pm 0,1\%$	$1 * 10^{11}$	$2 * 10^{12}$
(c)	$0,71 \pm 0,02$	$11,0 \pm 0,8$	$1,75 \pm 0,05$	1238 ± 69	$2,3 \pm 0,1\%$	$2 * 10^{11}$	$5 * 10^{12}$
(d)	$0,70 \pm 0,01$	$11,3 \pm 0,1$	$2,11 \pm 0,01$	1317 ± 69	$10,2 \pm 0,8\%$	$8 * 10^{10}$	$1 * 10^{12}$

The characteristical values prove, that PZT ceramic samples, which were not air-bindered and were sintered, show comparable dielectrical characteristics.

The results of table 4 are based on electromechanical vibration measuring with the aid of an impedance measuring bridge, whose evaluation from the parallel and serial resonance frequency f_p , f_s of the resonant circuit according

f_s = see page 14

permits to calculate for each vibration mode of the MLP sample of the effective coupling factor according

see page 14

Thereby, the proportion of the mechanical energy for the entire energy is indicated by $C_1/(C_0+C_1)$.

Table 4: Effective piezoelectrical coupling factors of the MLP samples from table 3 for two fundamental vibrations, determined from the measurement of each 3 MLP samples, sintered under the indicated conditions (a), (b), (c) and (d) in table 2.

MLP	Planar vibration			Consistency mode of vibration		
	f_s/kHz	f_p/kHz	k_{eff}	f_s/kHz	f_p/kHz	k_{eff}
(a)	158 ± 1	191 ± 2	$0,56 \pm 0,01$	3293 ± 15	3848 ± 79	$0,52 \pm 0,03$
(b)	166 ± 2	198 ± 4	$0,54 \pm 0,01$	2900 ± 78	3197 ± 25	$0,42 \pm 0,05$
(c)	163 ± 1	189 ± 5	$0,51 \pm 0,04$	2830 ± 111	3100 ± 108	$0,40 \pm 0,02$
(d)	154 ± 2	186 ± 2	$0,56 \pm 0,03$	2668 ± 36	3048 ± 47	$0,48 \pm 0,03$

The measurement of the Curie temperature at samples (c) showed a value of $339 \pm 2^\circ\text{C}$.

In fact, electromechanical coupling factors, which are in the area of the air-sintered samples, are accrued from the produced samples, sintered commonly under these conditions with copper.

The results of an excursion measurement on ceramic samples MLP are listed in table 5. The excursion Δh was determined parallelly to the polarized direction 3, in which the measuring voltage was set. The excursion measurement was carried out by inductive path measuring by setting up an electrical field E with a field strength of 2000 V/mm. Immediately before this measurement, the samples were impinged on by a field strength of 2000 V/mm in polarized direction, to rule out after-polarity effects and increased hysteresis because of the bedding after the polarity.

The relative density S of the ceramic samples MLP is calculated from the measured excursion Δh divided by the sample consistency h . From this the piezoelectrical coefficient d_{33} results according to the definition equation.

$$S_3 = d_{33} * E_3$$

d_{33} is a geometrically independent value for the piezoelectrical large signal characteristics of the examined ceramic.

Table 5: Excursion measurement of square ceramic samples ML: (edge length l, consistency h) with the composition according table 2 by setting a voltage of 2 kV/mm. Electrical measurement voltage U, excursion Δh and the piezoelectrical constant d_{33} are indicated.

Sample MLP	h/mm	U/V	$\Delta h/\mu m$	$d_{33} \cdot 10^{-12} m/V$
(a)	0,59+0,02	1180+4	0,88+0,01	747+10
(b)	0,70+0,01	1400+4	0,99+0,01	712+10
(c)	0,71+0,02	1420+4	1,03+0,06	723+40
(d)	0,70+0,01	1400+4	1,03+0,01	739+4

In case of printing on Cu-internal electrodes, a Cu-screen print paste proves to be advantageous, which shows a metal content as high as possible of approx. 75 m-% and is processed with a special high-polymer and thereby very viscous binder, which produces at already < 2m-%, related to the solid susbtance content, a viscosity as thixotrope as possible of > 2000 mPa·s. First, multilayer samples "VS" with up to 20 internal electrodes are produced for sample purposes. Starting from this, piezostacks with 100 to 300 Cu-internal electrodes are built up in a second step and are debindered and sintered under the mentioned conditions of a defined oxygen partial pressure in presence of steam.

The piezoceramic green foils are produced in a consistency, which produces, by considering the linear shrinkage during the sintering of typically 15%, a piezoceramic consistency from 20 to 200 μm . The Cu-electrodes have a layer consistency from 1 to 3 μm after the sintering.

Figure 2 shows partially a schematic cross section by a multilayer stack with alternating sequence of PZT ceramic foils and Cu-internal electrodes in 500 times (top) and in 1000 times (bottom) enlargement.

Figure 3 shows a measuring curve for the Cu-content of the also shown piezoceramic layer about the layer consistency after the sintering of a piezostack on the basis of the used original composition

$Pb_{10.97-y}Nd_{0.02}Cu_yV^{''0.01}(Zr_{0.54-z}Ti_{0.46+z})O_3$. It can be seen that the copper content in the ceramic layer dissolves, starting from the border. The calibration produces in the middle of the ceramic layer the minimal amount of $y = 0.001$. At the borders there is a 20 times higher value. Some lead oxyde is displaced from the combination by the into the Cu-ions diffused influence. The good connection of the Cu-internal electrodes to the ceramic is thereby proven.

The electrical characteristics of the multilayer ceramic components VS of the original composition

$Pb_{0.97}Nd_{0.02}V_{0.01}(Zr_{0.54}Ti_{0.46})O_3$ after the sintering at $1000^\circ C$ with 16 Cu-internal electrodes and for comparison with 20 Ag/Pd-internal electrodes (70/30) after the air-sintering at $1120^\circ C$ are indicated in table 6.

Table 6: Electrical characteristics of PZT multilayer ceramic samples VS on the basis of the original composition

$Pb_{0.97}Nd_{0.02}V^{''0.01}(Zr_{0.54}Ti_{0.46})O_3$: (a) powder pre-ground, medium grain size $d50\% = 0.53 \mu m$, 20 internal electrodes Ag/Pd (70/30), air-sintering at $1120^\circ C$, (c) powder finely ground, medium corn size $d50\% = 0.33 \mu m$, 16 Cu-internal electrodes, sintering at $1000^\circ C$ under inert conditions by N_2/H_2O steam.

Sample VS	Comments	C/nF	ϵ before polarization	ϵ after polarization	$\tan \delta$ after polarization	$\rho_{IS} \text{ Acm}^{-2}$ after polarization
(a)	Ag/Pd(70/30): Debinding/air-sintering $1120^\circ C$, Cu-finished.	125 ± 5	1104 ± 54	1561 ± 92	0,015	$7,9 \cdot 10^{-11}$
(c1)	Cu-internal electrodes: Debinding/sintering under N_2/H_2O steam, Cu-finished.	110 ± 4	908 ± 35	953 ± 37	0,027	$2,7 \cdot 10^{-10}$
(c2)	Cu-internal electrodes: Debinding/sintering under N_2, H_2O steam, Cu-finished.	114 ± 4	946	1013	0,026	$1,6 \cdot 10^{-10}$

Production of a piezo actuator from a ceramic of PZT type with Cu-internal electrodes.

For the production of piezo actuators with at first 160 Cu-internal electrodes, the green foils produced according to the method of the consistency from 40 to $50 \mu m$ are further processed according to the for multilayer ceramic condensators known standard method. The printing of the square cut PZT ceramic foils is done mechanically by screen printing technique (400 mesh) with the for piezo actuators common electrode design by usage of a commercial Cu-electrode paste. The stacking is done in a way, so that on each two non-printed foils a printed one follows. 100 piezo actuators in a green condition are received from the block after laminating by pressing or sawing.

The debinding is carried out corresponding to the in figure 1 shown temperature time diagram in the nitrogen stream by adding steam and hydrogen, so that there is a target value from $5 \cdot 10^{-2}$ to $2 \cdot 10^{-1}$ Pa for the O_2 partial pressure produced in the area of $500^\circ C$. Essentially lower oxygen partial pressures occur locally during the debinding. The ceramic is not subject to the reductive degradation in the temperature area of the debinding, because the equilibrated oxygen partial pressure is as well lowered, conditioned thermodynamically, and the reduction processes are kinetically sufficiently obstructed. The green parts of the

multilayer piezo actuators still show a residue content of carbon of 300 ppm after the debinding and are immediately afterwards ready to be sintered in the same set atmosphere, without causing a reductive degradation, which would lead to cracking, delamination and eventually to drifting of the internal electrodes because of the production of a low melting Cu/Pb-alloy.

Steam and forming gas are added to the nitrogen flux ($N_2 + 5\% H_2$). The dissociation of the steam according to



is used for setting a certain oxygen partial pressure. Corresponding to the law of mass action

$$K_D = \frac{p(O_2)^{\frac{1}{2}} \cdot p(H_2)}{p(H_2O)}$$

a certain oxygen partial pressure is thereby determined at a given temperature for a defined partial pressure ratio of steam and hydrogen. The calculation of the thermodynamic data produces the in figure 5 shown run of the curves for different H_2/H_2O ratios of concentration.

Normally the gas composition is selected in such a way, that the requested oxygen partial pressure is produced at sinter temperature T_{Sinter} . This condition is for example marked in figure 5 by *. Starting from this value the $p(O_2)$ runs parallel to the other curves with decreasing temperature. But this means, that the $p(O_2)$ value lies too low for $T < T_{Sinter}$, which is tolerable because of kinetic reasons, if necessary. The gas control curve Cu1 according to table 7 corresponds to this way of process. The equilibrium of Pb/PbO falls thereby already short starting at approx. 900°C, conditioned by the narrow thermodynamic window, through which metallic lead is produced if there is sufficient kinetic activity.

Alternatively to this, $p(O_2)$ was set in steps with different forming gas dosage corresponding to the gas control Cu2, the actual course of the oxygen partial pressure lies thereby until 400°C in the thermodynamic window. This way of process is good for the little reductive solid PZT mixture. The used adjustments Cu1 and Cu2 for the gas control are indicated in table 7. Figure 5 shows the calculated course of the partial pressure for the different ratios of concentration of the gases.

Table 7: Gas control Cu1 and Cu2

	Cu1	Dosage	Cu2	Dosage
N_2	Entire sintering	90 l/h	Entire sintering	1200 l/h
H_2/H_2O	Entire sintering	40 g/h	Entire sintering	100 g/h
$N_2 + 5\% H_2$	Entire sintering	256 ml/h	25 - 650°C	25 ml/h
			650 - 900°C	85 ml/h
			900 - 1000°C	200 ml/h
	Dewing point 36°C		Dewing point 36°C	

The sinter profile is as follows: The holding time at maximal temperature lies between 2 and 12 h. The heating up ramp and the cooling down ramp are traveled through with 5 K/min, the actuators are slowly heated up with 1 K/min. The in steps adjusted set-up of the oxygen partial pressure (figure 5) runs in conformity with the temperature curve, which is obtained by

an alteration of the forming gas flow meter. Thereby the steam partial pressure (100 g/h) is constant.

The obtained ceramic is tightly sintered to > 96% and shows mostly homogenous low porosity. The sinter grains grow to a for the piezoelectrical characteristics advantageous medium grain size of 0.8 – 5 µm.

Intact crack-free actuators are obtained. Their sequence of the internal electrodes and PZT ceramic layers is shown in a section in figure 2. The medium grain size in the ceramic structure is $d_{50} = 1,6 \pm 0,3 \mu\text{m}$. It lies thereby in a for the formation of piezoelectrical active domaines advantageous area.

The piezo actuators are ground and polished for the finishing and contacted in the area of the exiting internal electrodes with a for such applications common Cu-paste and and burned-in at 935°C according to a preset temperature time curve. The piezo actuators respond to the electrical measuring after the application of wires by the common Bond-technology.

The diagram of an excursion curve for a polarized PZT-piezoactuator with 160 Cu-internal electrodes is represented in figure 4. A density of 0,123% is produced by a voltage setting of 140,6 Volt at a consistency of 70 µm of the PZT ceramic layers. The piezoelectrical coefficient in direction to the applied field d_{33} is $614,6 \cdot 10^{-12} \text{ m/V}$.